

Investigating Missing Sources of Sulfur

Richard E Peltier & Kabindra M. Shakya
University of Massachusetts, Amherst

“Missing” Sulfur

- Begins with NAAMC in Nashville.



Photo Credit: Fairbanks North Slope Borough

Why investigate sulfur?

United States Court of Appeals
FOR THE DISTRICT OF COLUMBIA CIRCUIT

No. 08-1200 **September Term, 2013**

EPA-73FR16436
EPA-73FR16436-01

Filed On: December 11, 2013

State of Mississippi,
Petitioner

v.

Environmental Protection Agency,
Respondent

County of Nassau, et al.,
Intervenors

Consolidated with 08-1202, 08-1203, 08-1204,
08-1206

BEFORE: Tatel, Brown, and Griffith, Circuit Judges

ORDER

Upon consideration of the petition of the petitioners' American Lung Association, et al., for panel rehearing joined by the State petitioners, and the responses thereto, it is

No. 05-1120

In the Supreme Court of the United States

COMMONWEALTH OF MASSACHUSETTS, ET AL.,
PETITIONERS

v.

ENVIRONMENTAL PROTECTION AGENCY, ET AL.

ON WRIT OF CERTIORARI
TO THE UNITED STATES COURT OF APPEALS
FOR THE DISTRICT OF COLUMBIA CIRCUIT

BRIEF FOR THE FEDERAL RESPONDENT

PAUL D. CLEMENT
Solicitor General

No. 99-1257

In the Supreme Court of the United States

CAROL M. BROWNER, ADMINISTRATOR OF THE
ENVIRONMENTAL PROTECTION AGENCY, ET AL.,
PETITIONERS

v.

AMERICAN TRUCKING ASSOCIATIONS, INC., ET AL.

ON PETITION FOR A WRIT OF CERTIORARI
TO THE UNITED STATES COURT OF APPEALS
FOR THE DISTRICT OF COLUMBIA CIRCUIT

PETITION FOR A WRIT OF CERTIORARI

SETH P. WAXMAN
Solicitor General
Counsel of Record

LOIS J. SCHIFFER
Assistant Attorney General

GARY S. GUZY
General Counsel

OCTOBER TERM, 2000 457

Syllabus

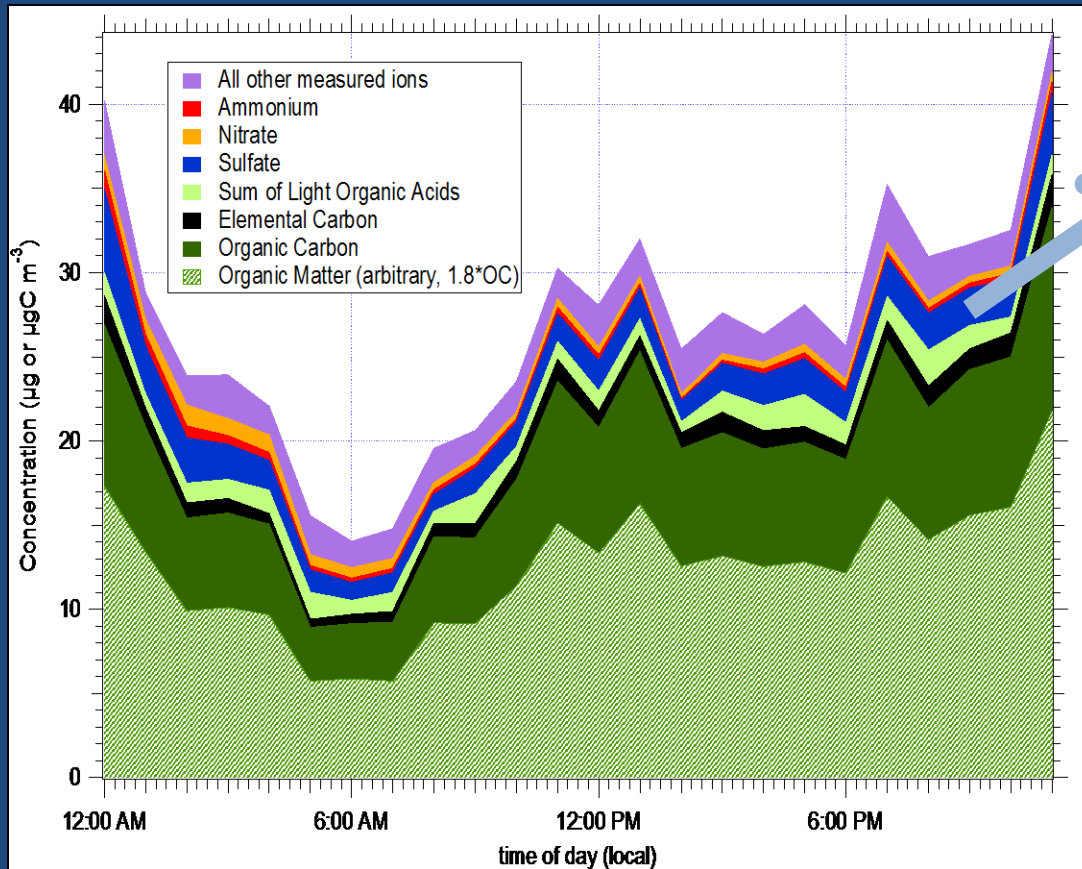
WHITMAN, ADMINISTRATOR OF ENVIRONMENTAL
PROTECTION AGENCY, ET AL. v. AMERICAN
TRUCKING ASSOCIATIONS, INC., ET AL.

CERTIORARI TO THE UNITED STATES COURT OF APPEALS FOR
THE DISTRICT OF COLUMBIA CIRCUIT

No. 99-1257. Argued November 7, 2000—Decided February 27, 2001*

Section 109(a) of the Clean Air Act (CAA) requires the Environmental Protection Agency (EPA) Administrator to promulgate national ambient air quality standards (NAAQS) for each air pollutant for which "air quality criteria" have been issued under § 108. Pursuant to § 109(d)(1), the Administrator in 1997 revised the ozone and particulate matter NAAQS. Respondents in No. 99-1257, private parties and several States (hereinafter respondents), challenged the revised NAAQS on

Winter diurnal profile in Fairbanks

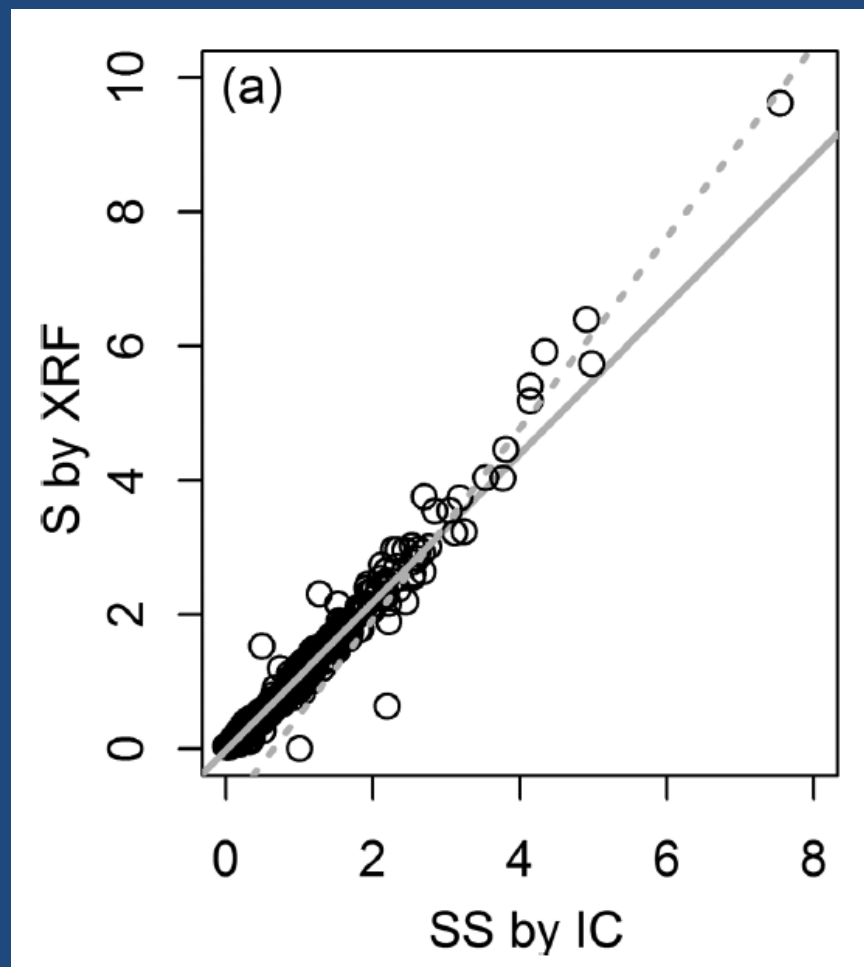


Very small
fraction of
total PM
burden



Sulfur: 2005-2012

- Thought to be (mostly) ammonium sulfate.
- If so, sulfur as sulfate should equal elemental sulfur by XRF. Right?



AQS Site ID: 20900010, Fairbanks, AK

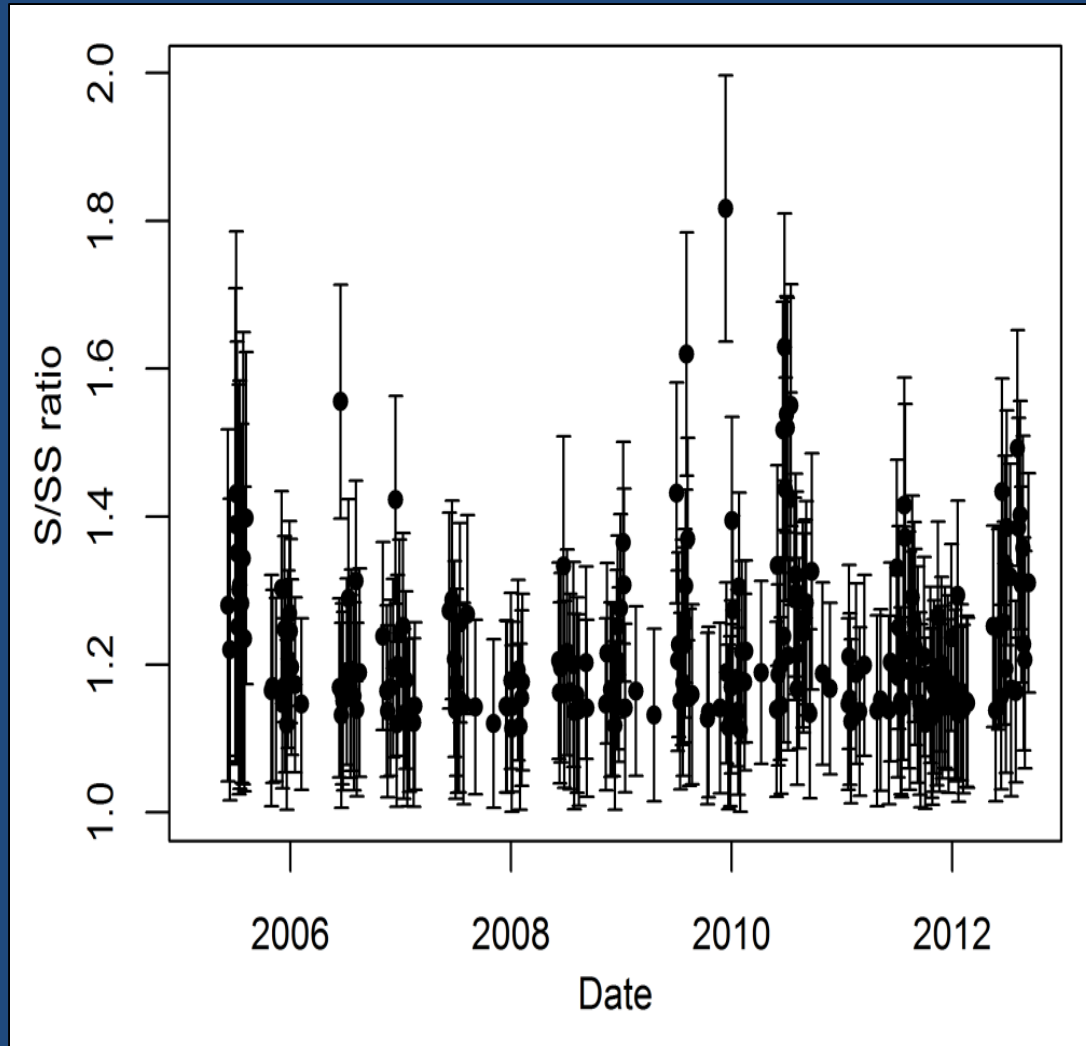
Method Background

- All measurements have error and uncertainty.
- E.g. 5.0 is really 5.0 ± 0.3 , or anywhere between 4.7 and 5.3
- As a result, a measure of $5.0 (\pm 0.3)$ by one method isn't always the same as a result of 5.0 ± 0.3 by another method
- Sulfur measured by two distinct analytic approaches: XRF and Ion chromatography



Results

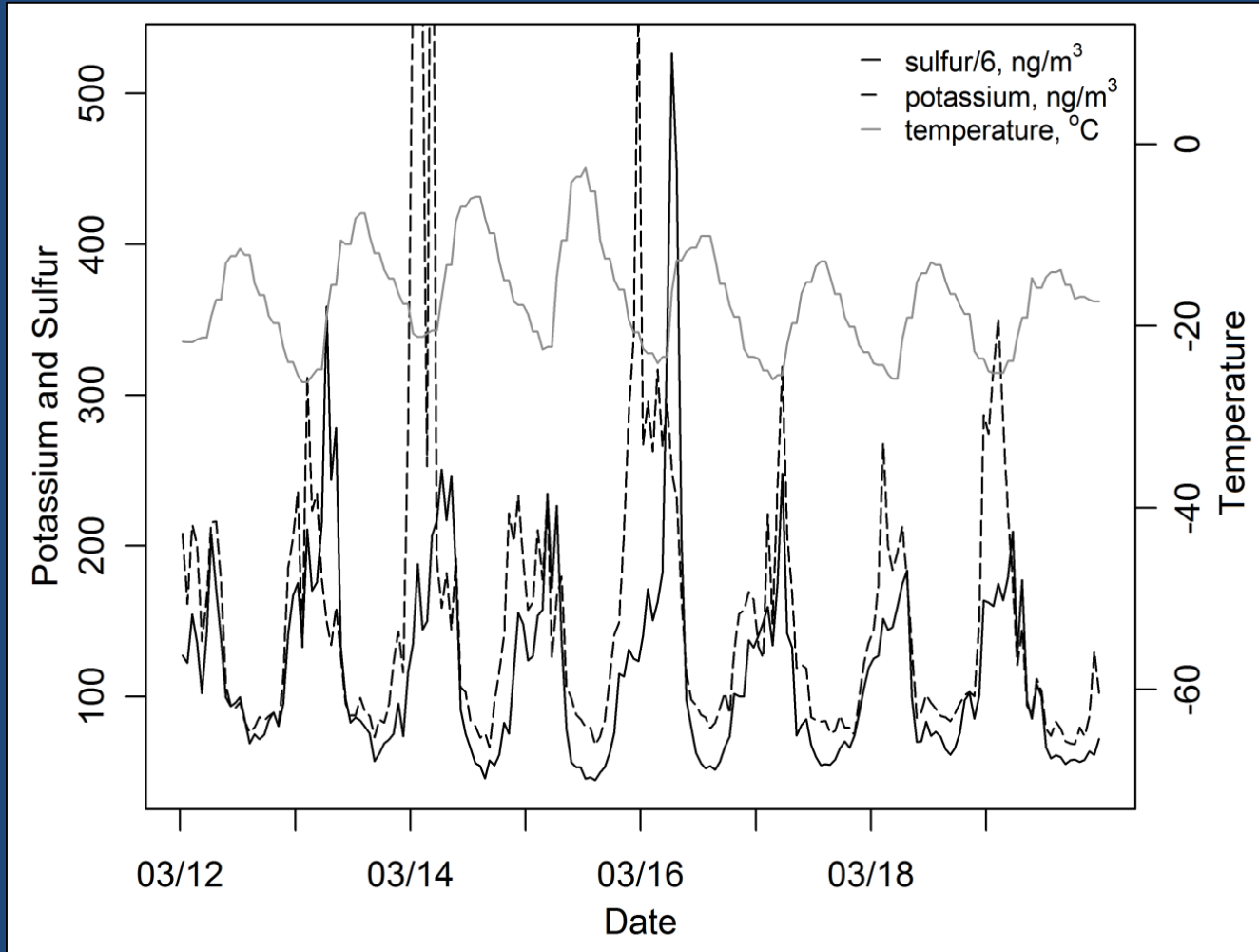
- N=235, LSqR slope of 1.22 (out of 831 measurements analyzes; LSqR slope of 1.16)



Source of 'excess' sulfur

- Most likely: organosulfur
 - High OC levels in Fairbanks, especially in winter
- S/SS ratios most correlated with OC, EC, Zn, NH_4^+ , and NO_3^- ; best agreement during cold temps.
- In 54% of observations, aerosol is acidic; inadequate ammonium for neutralization.
- Photochemistry can't be excluded.

Higher time resolution: Xact 625



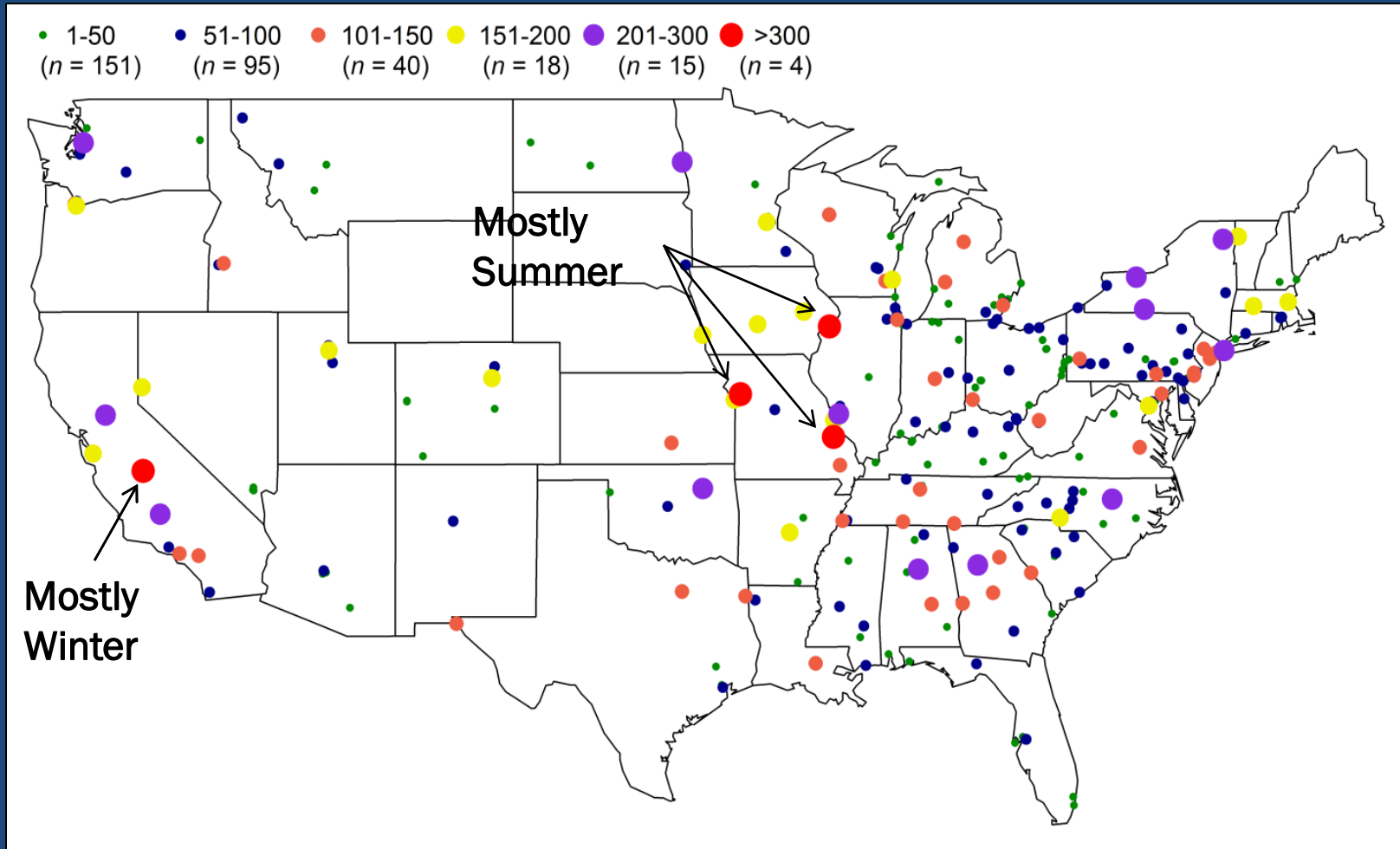
Fairbanks Summary

- Highest number of events in summer.
- Likely linked to OC (even with 10x lower OC concs in summer)
- Some indications linked to fuel oil (but tough to tease out due to high covariability)

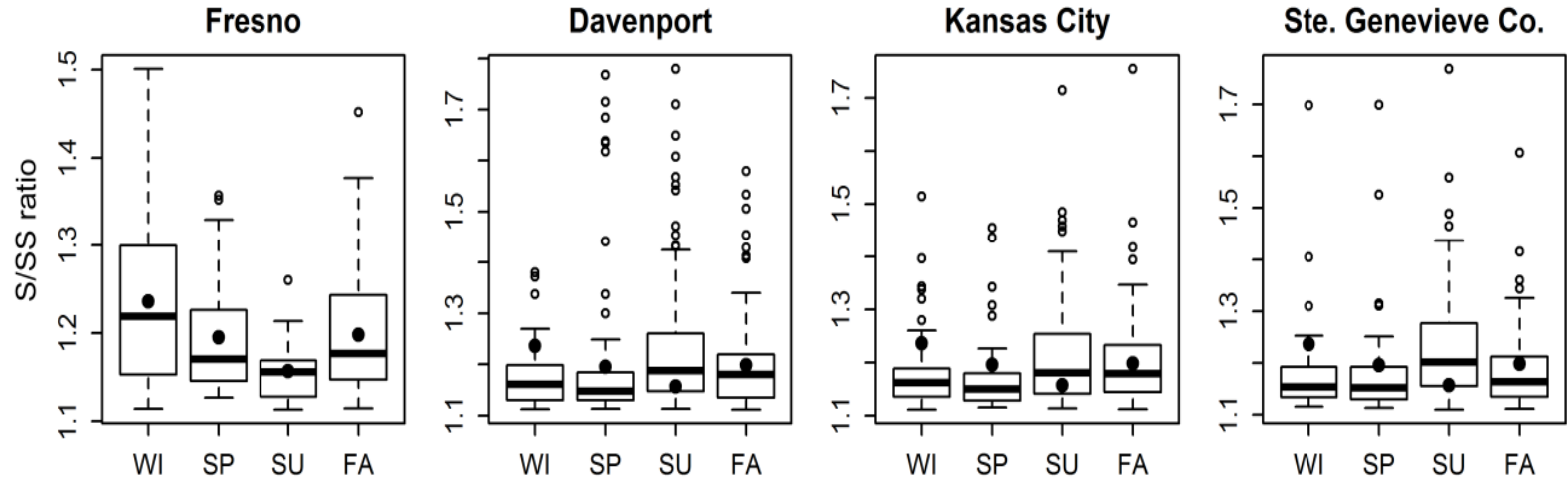
Beyond Fairbanks

- Polled data from 308 sites from AQS
- Analyzed ~160,000 sets of S and SO₄ measurements
- Approx 45k S/SS ratios were significantly different than 1 (with 0.8% as gross outliers, which are excluded here)
- Interesting to note that about half of these findings are high, half are low.

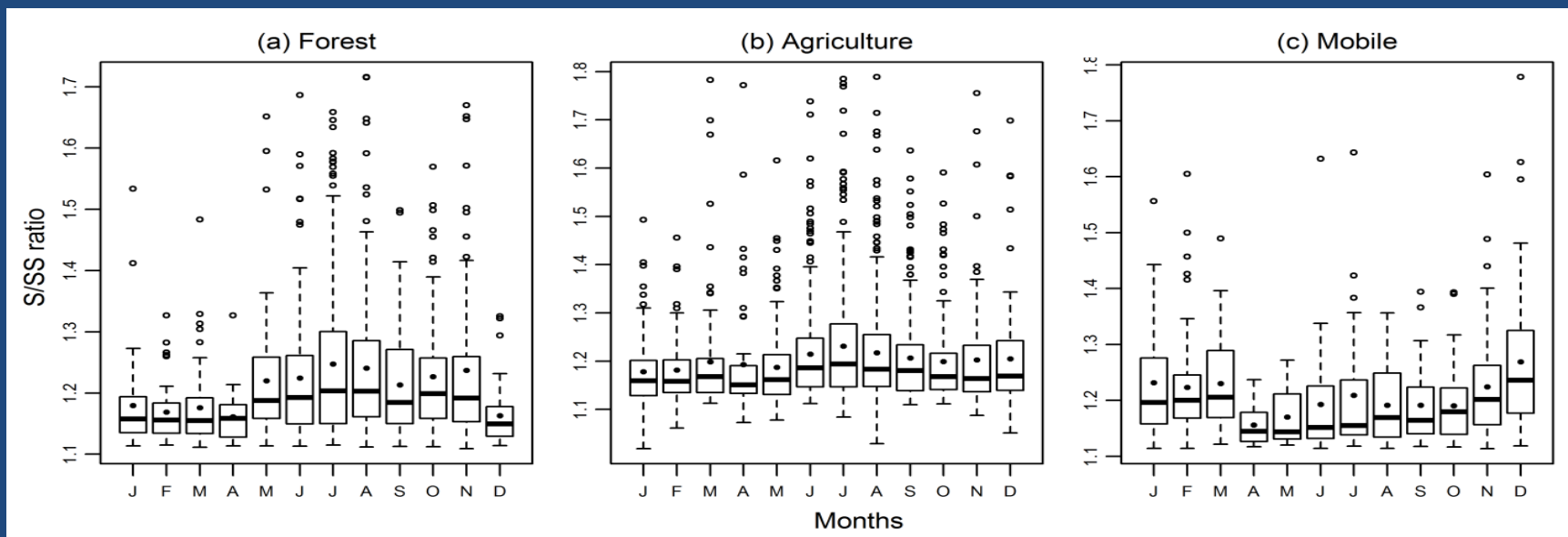
Spatial Distribution



Apparent seasonality



Seasonality by AQS site classification

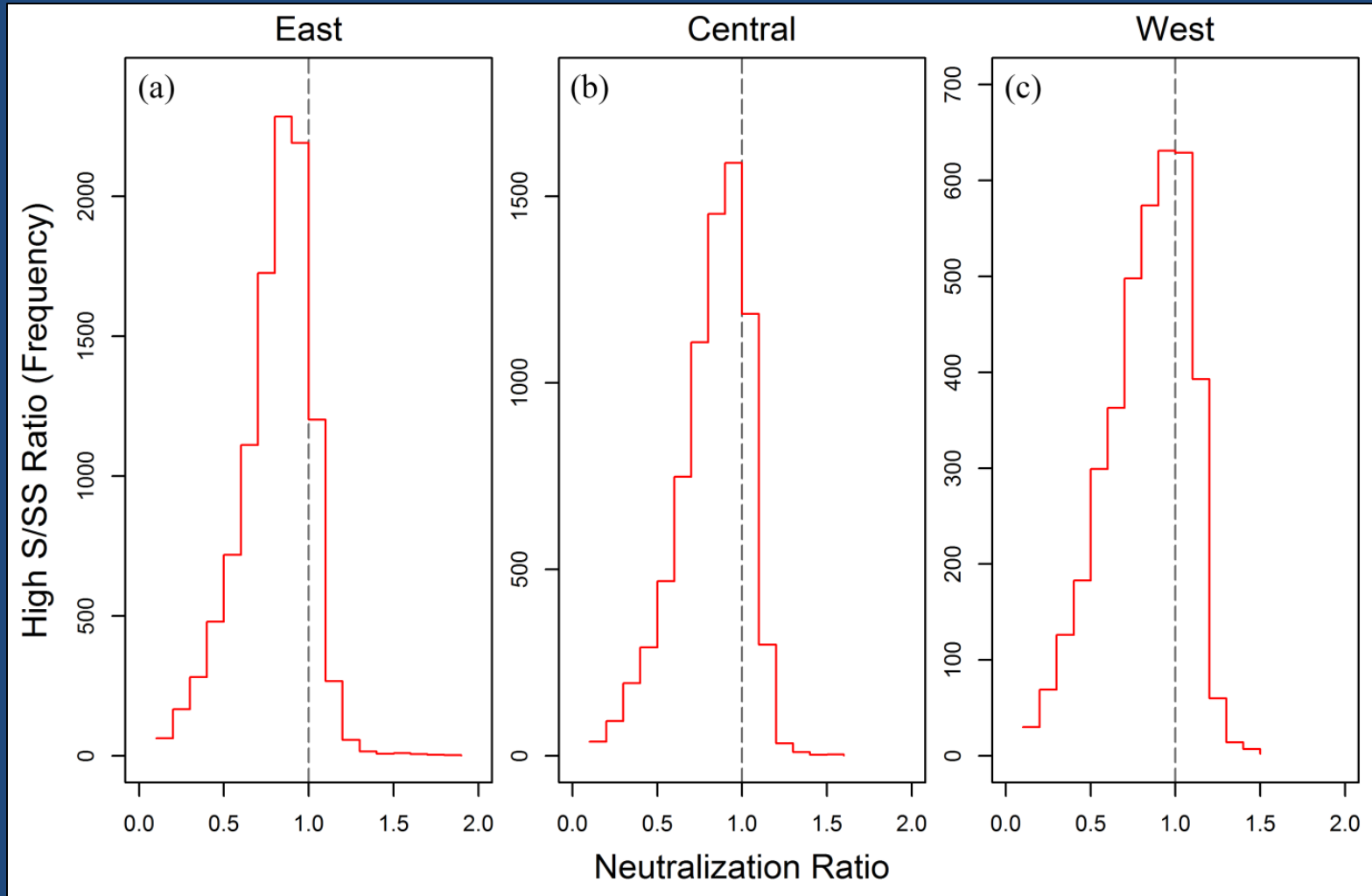


- At other site types, excess S much less frequently observed.

What does this mean?

- Probably a different formation mechanism across different locations
 - Or at least different sources requiring different mechanisms

Aerosol acidity by geography



Highest excess S to OC ratio

Site ID	Location	Landuse	Setting	Frequency	S/OC %	S/PM _{2.5} %
C.482011039.5	Deer Park, Houston-Sugarland, TX	Residential	Suburban	9	10	
C.482011039.6	Ibid.			94	10	1
C.483390089.5	Conroe, Houston-Sugarland	Commercial	Urban and Center City	13	10	2
C.050030005.5	Crossett, AR	Commercial	Urban and Center City	12	13	3
C.240030019.6	Fort Meade, Baltimore-Towson, MD	Commercial	Suburban	11	11	2
C.261150005.5	Luna Pier, Monroe, MI	Agricultural	Rural	73	11	2
C.540390011.5	Charleston, WV	Residential	Rural	143	10	2
C.390930016.5	Lorain, Cleveland-Elyria-Mentor, OH	Commercial	Suburban	8	13	2

All sites, except Crossett, AR, located within 80 miles of CFPP

Conclusions from National Dataset

- ‘Excess’ sulfur occurs across the US in both time and space.
- Accounts for as much as 13% of OC and ~2% of $PM_{2.5}$.
- Aerosol acidity important in summer; site proximity to mobile sources in winter.
- Less than one ratios suggest measurement error – over reporting by XRF or under reporting by IC.

(Partial) conclusions on sulfur

- *Real* excess sulfur occurs.
- Reinforces the critical importance of what you do.
- For communities on the cusp of attainment/non-attainment, might be a new low hanging fruit

Acknowledgements

- University of Massachusetts: Filimon Kiros
- Fairbanks North Slope Borough: Jim Conner, Barbara Trost, Adelia Falk, Todd Thompson, Kelly Shaw, Ron Lovell
- Cooper Environmental: Krag Pettersen
- Washington University: Jay Turner